

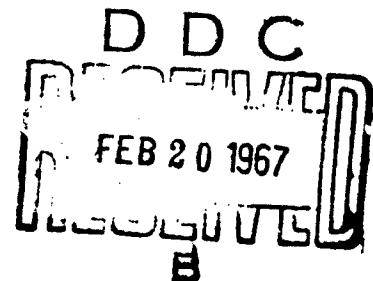
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# Critical Surface Tension for Spreading on a Liquid Substrate

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## ABSTRACT

A plot of the initial spreading pressures ( $F_{ba}$ ) or initial spreading coefficients ( $S_{ba}$ ) against the surface tensions of a homologous series of organic liquids  $b$  can be used to determine the critical surface tension for spreading ( $\gamma_c$ ) on a second substrate liquid phase  $a$ . Straight-line relations are found for various homologous series. The intercept of that line with the axis of abscissas ( $F_{ba} = 0$ , or  $S_{ba} = 0$ ) defines a value of  $\gamma_c$  for that series. This method is advantageous because it eliminates the need for measuring (or calculating) the contact angle of lens  $b$  floating on liquid  $a$ , it can be applied to any liquid substrate, and it is applicable even when  $\gamma_c$  does not lie within the range of surface tensions of the members of the homologous series of liquids  $b$ . The value of  $\gamma_c$  for the water/air interface has been determined in this way using several homologous series of pure hydrocarbon liquids. The lowest value found was 21.7 dynes/cm at 20°C for the n-alkane series. Higher  $\gamma_c$  values were obtained using olefins or aromatic hydrocarbons as the result of interaction between the unsaturated bond and the water surface. Since the results are analogous to those reported earlier for solid surfaces, it is concluded that the clean surface of water behaves as a low-energy surface with respect to low-polarity liquids. This result is to be expected if only dispersion forces are operative between each alkane liquid and water.

## PROBLEM STATUS

This is an interim report; work on this problem is continuing.

## AUTHORIZATION

NRL Problem C02-21  
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## CRITICAL SURFACE TENSION FOR SPREADING ON A LIQUID SUBSTRATE

### INTRODUCTION

The concept of a critical surface tension for spreading ( $\gamma_c$ ), originally developed from experiments on solid surfaces (1), was demonstrated by Jarvis and Zisman (2) to be applicable also to characterize the surface properties of liquids. For example, all members of a series of liquid fluoroesters with surface tensions of 19.7 dynes/cm or less were able to spread spontaneously on a liquid alkyl polyether substrate having a surface tension of 23.0 dynes/cm at 20°C, whereas those with surface tensions of 20.7 dynes/cm or more did not spread. Therefore, they estimated that the polyether surface had a value of  $\gamma_c$  midway between 19.7 and 20.7 dynes/cm. The largest value of  $\gamma_c$  determined for any liquid investigated by them was 29.0 dynes/cm for an aliphatic diester whose surface tension at 20°C was 30.1 dynes/cm. Since all of the fluorinated compounds, including those with surface tensions as high as 31.1 dynes/cm, spread on substrate liquids whose surface tension was 35.9 dynes/cm or higher,  $\gamma_c$  could not be determined for these substrate liquids. Thus, the method of Jarvis and Zisman was applicable only when a homologous series of spreading liquids could be found such that at least one member had a surface tension greater than the critical surface tension of the liquid substrate being investigated.

Johnson and Dettre (3) recently determined the critical surface tensions of several liquid fluorinated alcohols and of water. Their approach was to measure the surface and interfacial tension and with them to calculate the equilibrium contact angle ( $\theta$ ) of each of the *n*-alkane liquids by means of the Young equation. From a plot of  $\cos \theta$  vs the alkane surface tension ( $\gamma_b$ ), they obtained a value of  $\gamma_c$  of 19.1 dynes/cm for a clean water surface at 24.5°C.

A much more convenient method of measuring the value of  $\gamma_c$  of the surface of liquid *a* is based on a plot of the initial spreading coefficient ( $S_{ba}$ ) of liquid *b* on liquid *a* vs  $\gamma_b$ , the surface tension of liquid *b*, where *b* is a member of a homologous series of pure organic liquids. This method has two advantages over the preceding methods: first, it eliminates measuring (or calculating) the contact angle of a drop of liquid *b* in the presence of the deforming and obscuring meniscus of the substrate liquid *a*; second, it does not require that  $\gamma_c$  of liquid *a* should fall within the range of surface tensions exhibited by the collective members of the series of homologous spreading liquids. A recent report by Pomerantz, Clinton, and Zisman (4) has made available a rapid and reliable method for measuring  $S_{ba}$  from the initial spreading pressure  $F_{ba}$  for any liquid *b* which is able to spread spontaneously on *a*; in addition, they also have supplied a substantial amount of data on the spreading properties on water of many pure hydrocarbons.

By analogy with the results of past investigations of this Laboratory on liquid spreading upon solid substrates (1), each homologous series of spreading liquids would be expected to define a critical surface tension for spreading which should be a characteristic of the surface of liquid substrate *a*. When the interaction between liquid *b* and substrate liquid *a* arises solely from London dispersion forces, the critical surface tension of wetting would be the same, regardless of the homologous series used to supply the spreading liquid *b*. It is this common minimum value of  $\gamma_c$  in which we are most interested here. If liquid *b* adheres to *a* by other forces, such as hydrogen bonding, then that homologous series of *b* liquids would define a higher value of  $\gamma_c$ . We would expect graphs

of  $S_{ba}$  vs  $\gamma_b$  to be a series of lines, one for each homologous series, with each line displaced from the other by an amount which would be a measure of the contribution to the liquid/liquid adhesion arising from forces other than the dispersion forces. If the intercept at  $S_{ba} = 0$  for any one curve is used to determine  $\gamma_c$ , then  $\gamma_c$  would be greater, the stronger the nondispersion forces of adhesion.

If we desire to obtain the minimum possible intercept on the line  $S_{ba} = 0$ , we should use a homologous series of spreading liquids, no member of which has the ability to form either ionic or hydrogen bonds with the molecules in the surface of the liquid  $a$ . Hence when liquid substrate  $a$  is water, it is essential that liquid  $b$  should not ionize or form hydrogen bonds with water. Because there is much evidence for the hydrophilic character of the unsaturated carbon-carbon bond (4,5) and for its hydrogen-bonding ability (6), it is necessary to avoid unsaturated compounds and to use only the saturated hydrocarbons to determine the minimum value of  $\gamma_c$  for water.

### SPREADING OF THE ALKANES ON WATER AND RELATION TO $\gamma_c$

Since the surface tension of water much exceeds that of any organic liquid, it might be expected that organic liquids would always spread spontaneously over the clean surface of water. Nevertheless, many pure organic liquids, including numerous hydrocarbons, do not spread on water but form, instead, nonspreading lenses (7-9). As all of the  $n$ -alkanes below nonane spread spontaneously on water at 20°C (4,7,10),  $\gamma_c$  for water must lie between 21.8 and 22.9 dynes/cm, since these are the surface tensions of  $n$ -octane and  $n$ -nonane (11). A more precise determination of  $\gamma_c$  can be obtained if we plot  $S_{ba}$ , the initial spreading coefficient on water, as a function of  $\gamma_b$  for the  $n$ -alkane family of liquids. Until recently the only way to obtain  $S_{ba}$  was from the equation by which it was defined by Harkins (7-9), i.e.,

$$S_{ba} = \gamma_a - (\gamma_b + \gamma_{ab}). \quad (1)$$

When liquid  $b$  is nonspreading, it still is necessary to compute  $S_{ba}$  from Eq. (1). But when  $b$  spreads spontaneously on  $a$ , a much simpler approach is now available, because  $S_{ba}$  is usually equal to the initial spreading pressure ( $F_{ba}$ ) (4,10), which, in turn, can be measured conveniently by the "piston monolayer" method of Washburn and Keim (12). This method has several advantages, one of which is that only a few drops of pure liquid  $b$  are needed; a second is its lower sensitivity to the presence of impurities, as compared to interfacial tension measurements. This characteristic is well illustrated by the identical values of  $S_{ba}$  obtained seven years apart by two independent observers using different film balances, new sources of alkanes, and different methods of purification (4).

In Fig. 1 is a plot of  $S_{ba}$  vs  $\gamma_b$  for the lower  $n$ -alkanes on water at 20°C. These values of  $S_{ba}$  were obtained from Table 2 of Ref. 4. It will be seen that  $S_{ba}$  intercepts the axis  $S_{ba} = 0$  at  $\gamma_b = 21.9$  dynes/cm, which therefore is the value of  $\gamma_c$  for water at 20°C. Figure 2 is an analogous plot for the nonspreading members of the  $n$ -alkane family of liquids, based on the literature values of  $S_{ba}$  at 20°C shown in Table 1. A value of  $\gamma_c = 21.5$  dynes/cm can be determined by the intercept with the line  $S_{ba} = 0$ . A straight line provides a good fit to the data of Aveyard and Haydon (13) for  $S_{ba}$  vs  $\gamma_b$  for the four nonspreading, higher  $n$ -alkane homologs shown in Fig. 2, even though some curvature would be noted in a plot of their interfacial tension values as a function of  $N$ , the number of carbon atoms, for the series of alkanes from  $n$ -pentane through  $n$ -hexadecane.

Because a plot of  $S_{ba}$  vs  $\gamma_b$  should, in principle, be obtainable for some homologous series of organic liquids on any liquid substrate, we have at hand a general method of measuring  $\gamma_c$  for every liquid substrate. In practice the spreading pressure method is limited by the problem of finding a suitable piston monolayer for the particular liquid substrate. That the method is not restricted to the determination of  $\gamma_c$  for water is

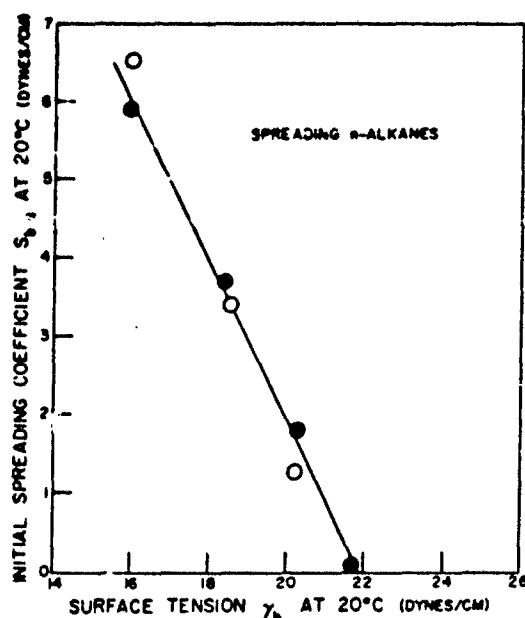


Fig. 1 - The initial spreading coefficient ( $S_{ba}$ ) as a function of the surface tension ( $\gamma_b$ ) of n-alkanes which spread on water. Filled symbols indicate data from Pomerantz, Clinton, and Zisman(4); open symbols indicate data from Aveyard and Haydon (13).

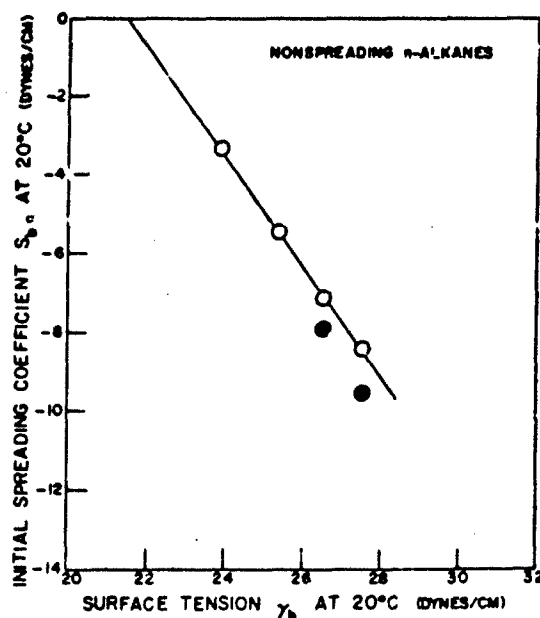


Fig. 2 - The initial spreading coefficient ( $S_{ba}$ ) as a function of the surface tension ( $\gamma_b$ ) of n-alkanes which do not spread on water. Open symbols indicate data from Aveyard and Haydon (13); filled symbols indicate data from Harkins (14).

evident from the investigation of Ellison and Zisman (19) in which values of  $S_{ba}$  were measured for an ethoxy-end-blocked silicone, two partially fluorinated organic silicates, and isopropanol when spreading on white mineral oil. A fluorochemical piston monolayer and an all-Teflon film balance were used.

The effect of branching in the hydrocarbon liquid on the value of  $\gamma_c$  for water was investigated by using other groups of homologous saturated hydrocarbons. Figure 3 is a plot made with the data obtained from Ref. 4. Note that all seventeen data points for the branched alkanes are displaced only slightly from those of the n-alkanes and that all but two of the points are well described by a straight line intercepting the zero axis of abscissas at  $\gamma_c = 22.5$  dynes/cm. As would be expected from the fact that the reversible work of adhesion for methyl groups is slightly larger than that of methylene groups (4), the data points closest to those of the unbranched alkanes are those of the branched alkanes containing the fewest methyl groups per molecule.

No case of spreading on water at ordinary temperature has been reported for any pure, saturated cyclic hydrocarbon (naphthenic), although at least fourteen naphthenics have been observed. Thus, using the Washburn and Keim method, Clinton (20) found negative spreading pressures for two homologous series of pure naphthenics (cyclopentane through n-butylcyclopentane and cyclohexane through n-butylcyclohexane). Lens formation has been reported for isopropyl bicyclohexyl and dicyclohexyl (21). Since the lowest value of  $\gamma_b$  for any of these compounds is 22.2 dynes/cm at 20°C found for methylcyclopentane by Robinson (22), it is apparent that  $\gamma_c$  must be less than 22.2 dynes/cm for this series of liquids. Reported values of  $S_{ba}$  of -8.54 and -11.17 dynes/cm (15) and of  $\gamma_b$  of 29.89 and 32.18 dynes/cm (23) for the cis and trans isomers of decahydronaphthalene, respectively, are consistent with this value of  $\gamma_c$ . This result is in good agreement

**Table 1**  
**Spreading Pressures and Related Properties for Various Hydrocarbons on Water**  
 (Data at 20°C unless otherwise specified)

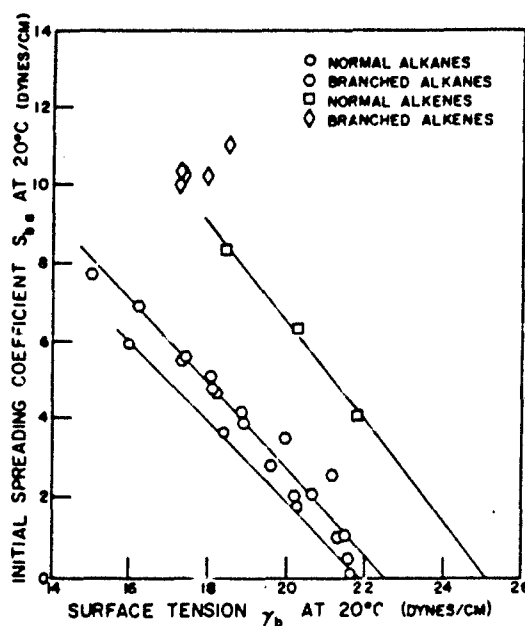
Hydrocarbon	Surface Tension $\gamma_b$ (dynes/cm)	Spreading Pressure $F_{ba}$ (dynes/cm)	Spreading Coefficient $S_{ba}$ (dynes/cm)	Interfacial Tension $\gamma_{ab}$ (dynes/cm)
<b>n-Alkanes</b>				
n-Nonane	22.92 (11)	< 0 (4)		
n-Decane	23.92 (11)	< 0 (4)	-3.35 (13)	52.30 (13) 51.24 (15) 52.30 (16) 52.0 at 24.5°C (3)
n-Dodecane	25.4 (11)	< 0 (4)	-5.41 (13)	52.78 (13) 52.8 at 24.5°C (3)
n-Tetradecane	26.53 (11) 25.6 (17)	< 0 (4)	-7.11 (13) -7.93 (14)	53.32 (13) 54.17 (14) 52.2 (17) 48.4 at 25°C (18)
n-Hexadecane	27.52 (11)	< 0 (4)	-8.44 (13) -9.56 (14) -9.52 (9, p. 104)	53.77 (13) 54.84 (14) 53.3 at 24.5°C (3)
<b>Aromatics</b>				
t-Butylbenzene	27.63 at 25°C (10)	5.3 (10)	5.2 (10)	39.3 at 25°C (10)
iso-Propylbenzene	27.71 at 25°C (10)	6.0 (10)	5.7 (10)	38.7 at 25°C (10)
sec-Butylbenzene	28.20 at 25°C (10)	4.7 (10)	4.7 (10)	39.2 at 25°C (10)
1,2,3,4-Tetrahydronaphthalene	36.02 at 25°C (10)	0.0 (10)	-2.5 (10)	38.6 at 25°C (10)

with the values of  $\gamma_c$  calculated previously for the n-alkane liquids. For the remainder of this discussion, we will assume  $\gamma_c = 22.0$  dynes/cm with respect to low-polarity liquids.

#### EFFECT OF UNSATURATED BONDS ON $\gamma_c$

As shown in Fig. 3, the introduction of unsaturation at the  $\alpha$ -position in the straight-chain alkanes resulted in a rectilinear graph of  $S_{ba}$  vs  $\gamma_b$  with almost the same slope as that exhibited by the n-alkanes but with an intercept of  $\gamma_c = 25.1$  dynes/cm. The difference of  $25.1 - 21.7 = 3.4$  dynes/cm is presumably a measure of the contribution to the observed

Fig. 3 - The effect of branching and unsaturation on the initial spreading coefficient ( $S_{ba}$ ) as a function of the surface tension ( $\gamma_b$ ) of acyclic hydrocarbons. All data are from Pomerantz, Clinton, and Zisman (4).



liquid/liquid adhesion resulting from forces between the water and olefinic double bond other than the dispersion forces. Pomerantz, Clinton, and Zisman (4) found by similar reasoning a difference of 4.2 dynes/cm representing the contribution of the double bond to  $S_{ba}$  when saturated and unsaturated hydrocarbons of the same boiling point range were compared.

The distribution of data points for the unsaturated branched alkanes in Fig. 3 is consistent with a straight-line relation but is not sufficient to determine its intercept with the axis of abscissas. A comparison of the relative positions of the data points for a saturated branched alkane and two related unsaturates, 2-methyl-pentane compared to 2-methyl-1-pentene and 4-methyl-1-pentene (see Tables 2 and 3 of Ref. 4), suggests that unsaturation in the branched alkanes may increase the apparent value of  $\gamma_c$  by 5 dynes/cm.

The effect of aromatic and olefinic unsaturation on  $\gamma_c$  can be compared, and for this purpose use was made of the data on the n-alkyl benzenes in Tables 3 and 4 of Ref. 4. A graph of the value of  $S_{ba}$  vs  $\gamma_b$  was of no help in calculating  $\gamma_c$ , because  $\gamma_b$  varied too little in this series of compounds. However, a graph of  $S_{ba}$  versus the number of carbon atoms in the alkyl chain revealed that  $S_{ba}$  approaches zero at the homolog n-hexyl benzene; hence  $\gamma_c$  must be about equal to  $\gamma_b$  for n-hexyl benzene or about 30 dynes/cm. When additional phenyl groups were present in the liquid molecule,  $\gamma_c$  was even higher. Among the hydrocarbons containing more than one phenyl group, liquids with surface tensions as high as 37 dynes/cm have been reported by Harkins and Feldman (7) to exhibit initial spreading prior to lens formation, as well as small positive spreading coefficients. The increase in  $\gamma_c$  of some 7 or more dynes/cm upon the introduction of a second phenyl group is consistent with the value of about 8 dynes/cm resulting from the introduction of the first phenyl group.

A comparison of the spreading behavior on water of cyclohexane ( $F_{ba} = -3.2$  dynes/cm at 20°C (15)) and of benzene (Table 4 of Ref. 4) is revealing. Cyclohexane ( $\gamma_b = 24.95$  dynes/cm at 20°C (11)) is nonspreading on water and it belongs to the group of naphthenic liquids for which  $\gamma_c$  of water is 22 dynes/cm. The surface tension of benzene (28.88 dynes/cm at 20°C) exceeds that of its saturated counterpart by 3.9 dynes/cm and exceeds the minimum value of  $\gamma_c$  of water (21.7 dynes/cm average for unbranched, saturated hydrocarbons) by 7.2 dynes/cm; nevertheless, benzene spreads spontaneously over water



and has a large positive value of  $S_{ba}$ . The difference in  $S_{ba}$  for these two liquids is 13.0 dynes/cm, although their liquid surface tensions differ by only 3.9 dynes/cm. A comparison of the interfacial tension for the system benzene/water (34.1 dynes/cm (4)) with that for cyclohexane/water (51.0 dynes/cm(10)) reveals a difference in  $\gamma_{ab}$  of 16.9 dynes/cm, which is about four times as large as that for the systems hexene-1/water vs hexane/water (46.0 vs 50.8 dynes/cm (4)). Therefore, the decrease in  $\gamma_{ab}$  upon introduction of the resonating aromatic system of three double bonds was approximately four times that caused by the introduction of one alpha olefinic double bond.

Comparison of the data given previously for decahydronaphthalene (15,23) and in Table 1 for 1,2,3,4-tetrahydronaphthalene indicates that the substitution of an aromatic for a saturated ring in one half of a fused ring system is sufficient to increase  $\gamma_c$  by 12 dynes/cm, if it is assumed that the data point for the nonspreading aromatic compound falls on a line with the same slope as that for the nonspreading naphthenic hydrocarbons. In this case, however, the difference in  $\gamma_{ab}$  corresponds to 13 dynes/cm or less when aromaticity is introduced in the condensed ring compound. It is no surprise that the effect of aromaticity on  $\gamma_c$  is not uniquely determinable, since the forces additional to dispersive forces will depend not only on the number of aromatic rings present, but also on the ease with which the aromatic ring can orient with its plane face parallel to and in contact with the surface of the water at one extreme or with the aromatic ring of an adjacent organic molecule at the other extreme. Thus, steric considerations must influence the interaction of the aromatic ring with the substrate.

#### GENERAL REMARKS

Table 2 summarizes the values of  $\gamma_c$  for water and other liquid substrates obtained by the several methods employed to date. Our value of  $\gamma_c$  of 22 dynes/cm for water is consistent with all the results obtained for the three types of organic liquids which have low polarity and are not capable of interacting through hydrogen bonding with the underlying water surfaces, i.e., n-alkanes, branched alkanes, and naphthenics. Thus, bulk water is shown to be a low-energy surface when the organic liquids are limited to those which only have dispersion forces operating to make them adhere to the water surface. Moreover, the value of  $\gamma_c = 22$  dynes/cm is in accord with the calculated dispersion component  $\gamma^d = 21.8 \pm 0.7$  dynes/cm obtained by Fowkes (24) for the surface of bulk water at 20°C. This agreement is significant, since it is tantamount to stating that the surface field of force of bulk water can be treated as comprising only an additive dispersion energy and a hydrogen-bonding energy contribution. Johnson and Dettre's significantly lower value of  $\gamma_c = 19.1$  dynes/cm at 24.5°C (3) is difficult to explain, since one would not expect the 4.5°C increase in temperature to cause such a decrease in  $\gamma_c$ . Indeed, the temperature coefficients of  $\gamma_h$  and  $\gamma_{ab}$  reported by Aveyard and Haydon (13) indicate a decrease in  $\gamma_c$  of only 0.7 dyne/cm for a 10°C rise in temperature.

The experimental basis for the straight-line relationship obtained between  $S_{ba}$  and  $\gamma_b$  for the clean surface of water is the near constancy of  $\gamma_{ab}$  and the nearly linear behavior of  $\gamma_h$  for the homologous families of alkanes, 1-alkenes, and n-alkyl benzenes, when  $N$  is not too large. This experimental independence of  $\gamma_{ab}$  from  $\gamma_h$  has been established by many measurements on liquid/liquid systems and is illustrated by Figs. 3 and 4 of Ref. 4. A straight-line relation would be expected, since  $S_{ba}$  is equal to the difference between the reversible work of adhesion ( $W_{ba}$ ) and the work of cohesion ( $W_{bb}$ ). The first term is proportional to  $N$ , provided the adsorbed hydrocarbon molecules lie in the plane of the water surface, and the second term is also linearly related to  $N$  when  $N$  is not large.

The evidence presented here for the low-energy character of the surface of liquid water with respect to low-polarity liquids is in agreement with results reported by us recently (21) on the effect of increased water vapor adsorption on glass in reducing its wettability by hydrophobic organic liquids and its critical surface tension ( $\gamma_c$ ). It was

Table 2  
Comparison of the Critical Surface Tension for Spreading ( $\gamma_c$ ) with the  
Liquid Surface Tension ( $\gamma_a$ ) for Various Low-Energy Liquids

Substrate Liquid	Temp. (°C)	Surface Tension $\gamma_a$ (dynes/cm)	Critical Surface Tension $\gamma_c$ (dynes/cm)	Ref.
$F(CF_2)_2CH_2OH$	24.5	17.4	13.2	3
Ucon fluid DLB 44E (a double end-blocked polypropylene oxide)	20	23.0	20.2	2
$H(CF_2)_4CH_2OH$	24.5	23.8	17.5	3
$H(CF_2)_2CH_2OH$	24.5	26.0	17.8	3
n-Hexadecane	20	27.3	23.1	2
Mineral oil (light petrolatum)	20	29.9	23.8	2
Squalene	20	31.4	26.7	2
Bis(2-ethylhexyl)sebacate	20	30.1	29.0	2
Nitromethane	20	35.9	> 31.1	2
Alkazene 42 (1,2-dibromoethylbenzene)	20	38.3	> 31.1	2
1-Methylnaphthalene	20	38.4	> 31.1	2
Tricresyl phosphate	20	40.4	> 31.1	2
Propylene carbonate	20	41.0	> 31.1	3
Phosphen 4 (a phenoxy bis(o-chloro-phenoxy)phosphate)	20	43.5	> 31.1	2
Aroclor 1248 (a trichlorobiphenyl)	20	43.7	> 31.1	2
Water	24.5	72.1	19.1	3
	20	72.8	21.7	This report

found that  $\gamma_c$  decreased markedly during the formation of the first adsorbed monolayer of water and reached a minimum value at a duplex film which, in turn, was somewhat above the value of  $\gamma_c$  for bulk water given here.

The fact that  $\gamma_c$  is as low as 22 dynes/cm for the alkanes spreading on water deserves interpretation in terms of the surface structure of water. Obviously, when water is in contact with an alkane or other nonhydrogen-bonding liquid, the molecules of water in the interface will be oriented to make the free surface energy a minimum. The highly associated nature of liquid water makes it difficult to determine that surface configuration. It is surely not the result of the oriented adsorption of monomeric water.

Stevenson (25) has concluded from infrared absorption data that fewer than 1% of the molecules of liquid water at ordinary temperatures exist in a nonhydrogen-bonded state. Timmons and Zisman (26) have recently shown that liquid water at 2°C behaves in contact angle hysteresis experiments as if it were comprised on the average of aggregates of six monomers. It is suggested that the adsorbed species at the alkane/water interface is comprised of these or similar associated clusters so organized and oriented as to minimize the surface energy. It is interesting that Adamson and Dormant (27) have recently reported that ice acts like a low energy surface with respect to the adsorption of nitrogen at 78°K, and they have concluded that the hydrogen atoms in the ice surface are outermost and are not in the relatively polar form of hydroxyl groups.

The value of 22 dynes/cm for the critical surface tension of water is much less than the surface tension of water (72.8 dynes/cm at 20°C). While  $\gamma_c$  must correlate with (be symbatic with) the surface energy  $\gamma_a$  of a liquid, or  $\gamma_{s^0}$  of a solid, the above result again emphasizes what has been carefully pointed out previously by Fox and Zisman (28), namely, that it is not valid to equate  $\gamma_c$  to  $\gamma_{s^0}$ . That this admonition is equally applicable to liquid surfaces (whether organic or aqueous) is illustrated by the tabulation of  $\gamma_c$  and  $\gamma_a$  values from the literature in Table 2.

Moreover, since the surface energy can be determined experimentally for a liquid, the extent to which  $\gamma_c$  is not a measure of the surface energy can be shown graphically, as in the plot of  $\gamma_c$  vs  $\gamma_a$  in Fig. 4. Here the dotted construction line (line B) indicates

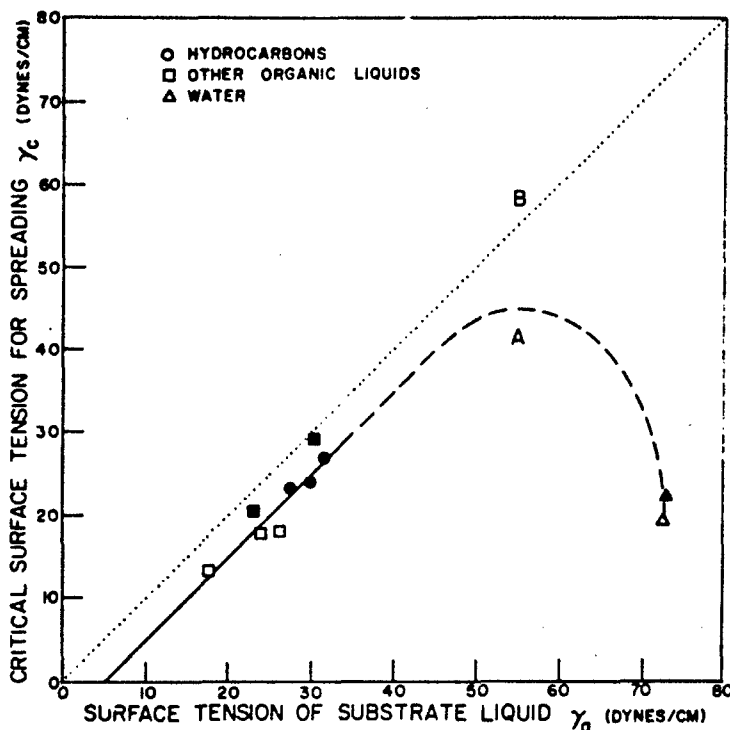


Fig. 4 - The relation of the critical surface tension for spreading ( $\gamma_c$ ) to the surface tension ( $\gamma_a$ ) of the substrate liquid. Filled symbols indicate data at 20°C from this report and from Jarvis and Zisman (2); open symbols indicate data at 24.5°C from Johnson and Dettre (3).

what the relation would be if  $\gamma_c$  were equal to the free surface energy or surface tension ( $\gamma_a$ ). The relation determined experimentally is indicated by the data points representing the results for the several liquids at either 20°C or 24.5°C as given in Table 2; since the temperature difference is small, it is not expected to affect the results significantly. From the positions of the data points for the three hydrocarbon liquids relative to line B, it is apparent that the dispersion energy  $\gamma^d$  (as measured by  $\gamma_c$ ) represents a major fraction of the free surface energy of these compounds; similar considerations apply to the remaining five organic liquids. In the case of water, however,  $\gamma^d$  (as measured by the minimum value of  $\gamma_c$ ) is a much smaller fraction of the free surface energy, and the difference is presumed to be the contribution arising from hydrogen-bonding energy between adjacent water molecules. Thus, when values of  $\gamma_c$  greater than the minimum value are obtained (for different liquid series on water), the excess must represent the net effect of both the change of forces operating across the interface (due to dipole-dipole interaction, increased induced polarization, hydrogen-bonding, etc.) and the alteration of forces between the adjacent water molecules (due to molecular reorientation, variation in cluster size, etc.).

Figure 4 suggests that the data point for water could be connected to those for the organic liquids by a curve (such as curve A) which recedes away from line B the greater the nondispersion-force contribution to the surface free energy. Since hydrogen bonding is prevalent in most organic liquids having surface tensions above 50 dynes/cm, a portion of curve A has been dashed in to suggest the relation for such liquids; the continuous portion of the curve indicates the relation determined experimentally for liquids of surface tensions below about 30 dynes/cm. Experimental data on  $\gamma_c$  for liquids of high surface tension and strong hydrogen bonding are needed; the data in Table 2 for liquids with surface tensions above 30 dynes/cm indicate that such a determination is experimentally feasible.

## REFERENCES

1. Zisman, W.A., "Relation of the Equilibrium Contact Angle to Liquid and Solid Constitution," pp. 1-51 in "Advances in Chemistry Series, No. 43," Washington:Am. Chem. Soc., 1964
2. Jarvis, N.L., and Zisman, W.A., J. Phys. Chem. 63:727 (1959)
3. Johnson, R.E., Jr., and Dettre, R.H., J. Colloid Interface Sci. 21:610 (1966)
4. Pomerantz, P., Clinton, W.C., and Zisman, W.A., "Spreading on Water, Interfacial Tension and Adhesional Energy of the Lower Alkanes, Alkenes, and Alkyl Benzenes," NRL Report 6495, in progress; presented at the 152nd Annual Meeting, American Chemical Society, Division of Colloid and Surface Chemistry, New York City, Sept. 12, 1966
5. Cary, R., and Rideal, E.K., Proc. Roy. Soc. (London) A109:306 (1925)
6. Pimentel, G.C., and McClellan, A.L., "The Hydrogen Bond," p. 202, San Francisco: W. H. Freeman, 1960
7. Harkins, W.D., and Feldman, A., J. Am. Chem. Soc. 44:2665 (1922)
8. Harkins, W.D., J. Chem. Phys. 9:552 (1941)
9. Harkins, W.D., "The Physical Chemistry of Surface Films," pp. 29, 44, 99, 104, New York:Reinhold, 1952
10. Shewmaker, J.E., Vogler, C.E., and Washburn, E.R., J. Phys. Chem. 58:945 (1954)
11. Quayle, O.R., Chem. Reviews 53:439 (1953)
12. Washburn, E.R., and Keim, C.P., J. Am. Chem. Soc. 62:1747 and 2318 (1940)
13. Aveyard, R., and Haydon, D.A., Trans. Farad. Soc. 61:2255 (1965)
14. Harkins, W.D., "Determination of Surface and Interfacial Tension," Chap. IX, p. 360 in "Physical Methods of Organic Chemistry," A. Weissberger, ed., New York:Interscience, 1949
15. Rose, W.E., and Seyer, F.W., J. Phys. Chem. 55:439 (1951)
16. Jasper, J.J., and Seitz, H.R., J. Phys. Chem. 63:1429 (1959)
17. Girifalco, L.A., and Good, R.J., J. Phys. Chem. 61:904 (1957)
18. Hutchinson, E., J. Colloid Sci. 3:235 (1948)
19. Ellison, A.H., and Zisman, W.A., J. Phys. Chem. 60:416 (1956)
20. Clinton, W.C., NRL, private communication

21. Shafrin, E.G., and Zisman, W.A., "The Effect of Adsorbed Water Vapor upon the Spreading of Organic Liquids on Soda-Lime Glass," NRL Report 6496, in progress; presented at the 151st Annual Meeting, American Chemical Society, Division of Colloid and Surface Chemistry, Pittsburgh, Pa., March 25, 1966
22. Robinson, A.E., Jr., Ph.D. Thesis at Emory Univ., Dissert. Abstr. 19:2447 (1959), L.C. Card No. Mic 58-5177
23. Seyer, W.F., and Davenport, C.H., J. Am. Chem. Soc. 63:2425 (1941)
24. Fowkes, F.M., "Dispersion Force Contributions to Surface and Interfacial Tensions, Contact Angles, and Heats of Immersion," pp. 99-111 in "Advances in Chemistry Series, No. 43," Washington:Am. Chem. Soc., 1964
25. Stevenson, D.P., J. Phys. Chem. 69:2145 (1965)
26. Timmons, C.O., and Zisman, W.A., J. Colloid Sci. 22:165 (1966)
27. Adamson, A.W., and Dormant, L.M., J. Am. Chem. Soc. 88:2055 (1966)
28. Fox, H.W., and Zisman, W.A., J. Colloid Sci. 7:109 (1952)

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<p>A plot of the initial spreading pressures (<math>F_{ba}</math>) or initial spreading coefficients (<math>S_{ba}</math>) against the surface tensions of a homologous series of organic liquids <math>b</math> can be used to determine the critical surface tension for spreading (<math>\gamma_c</math>) on a second substrate liquid phase <math>a</math>. Straight-line relations are found for various homologous series. The intercept of that line with the axis of abscissas (<math>F_{ba} = 0</math>, or <math>S_{ba} = 0</math>) defines a value of <math>\gamma_c</math> for that series. This method is advantageous because it eliminates the need for measuring (or calculating) the contact angle of lens <math>b</math> floating on liquid <math>a</math>, it can be applied to any liquid substrate, and it is applicable even when <math>\gamma_c</math> does not lie within the range of surface tensions of the members of the homologous series of liquids <math>b</math>. The value of <math>\gamma_c</math> for the water/air interface has been determined in this way using several homologous series of pure hydrocarbon liquids. The lowest value found was 21.7 dynes/cm at 20°C for the n-alkane series. Higher <math>\gamma_c</math> values were obtained using olefins or aromatic hydrocarbons as the result of interaction between the unsaturated bond and the water surface. Since the results are analogous to those reported earlier for solid surfaces, it is concluded that the clean surface of water behaves as a low-energy surface with respect to low-polarity liquids. This result is to be expected if only dispersion forces are operative between each alkane liquid and water.</p>			

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Critical surface tension						
Filament wound construction						
Glass textiles						
Fibers						
Plastics						
Water						
Surface properties						
Organic compounds						
Liquids						
Spreading						
Hydrocarbons						
Alkenes						
Alkanes						
Surface tension						
Hydrogen bonding						
Adhesion						
Structure of water						